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The effects of instrument parameters and sample properties on thermal decomposition: interpreting thermal analysis data from Mars

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Abstract

Thermal analysis instruments have been used on Mars by the Viking, Phoenix, and MSL missions. These instruments can be very useful in identifying volatile-bearing minerals such as carbonates, sulfates, or phyllosilicates down to very low abundances. Mineral identification is done by comparing thermal decomposition behavior of samples with known mineralogy to samples with unknown mineralogy. However, thermal decomposition behavior can change with instrument conditions such as pressure and sample properties such as particle size. The Mars instruments flown to date have used much lower pressures and flow rates than traditional laboratory experiments. The objective of this work was to investigate whether an analytical model based on equilibrium thermodynamics can accurately predict changes in decomposition temperature in instruments operating under lower pressure/flow conditions. We find that while the model predicts the general trend that decomposition temperature drops with decreasing pressure, the difference between modeled and measured temperatures can be on the order of 100°C for carbonates and sulfates. These differences can be explained by factors such as sample particle size, carrier gas species, gas flow rate, and oven volume. A calcium carbonate sample shows how particle size can change decomposition temperature by almost 200°C (decomposition temperatures decrease with decreasing particle size) and that carrier gas species, flow rate, and instrument geometry can affect decomposition temperatures by 20-50°C. These results demonstrate that predicting changes in decomposition temperature based on a thermodynamic or empirical model is not sufficient and that samples must be run under instrument conditions relevant to the instrument that produced the data on Mars. Furthermore, the effects of particle size, carrier gas species and flow rate, as well as instrument geometry must be taken into account in order to compare Mars data to samples run in terrestrial labs. This work shows the magnitude of these factors, demonstrating why they must be taken into account, providing a framework for how to correctly interpret thermal analysis data from Mars.

Keywords: Mars; Viking; Phoenix; MSL; SAM; TEGA; Mineralogy; Thermal analysis; Thermal decomposition; Evolved gas analysis; PACS codes; Thermal analysis 81.70.Pg; Minerals; Physical properties of; 91.60.-x

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Background

The term thermal analysis (TA) is used to describe a variety of analytical techniques that involve sample analysis by heating. Thermal analysis has long been used to investigate the temperature, enthalpy, and kinetic parameters of decomposition reactions [1-3]. By measuring these parameters on a sample with known mineralogy, a mineralogical fingerprint is established that can be used to identify that mineral in a sample of unknown composition. An understanding of how thermal analysis is used for mineral identification is important to Mars scientists because TA instruments have been used on Viking, Phoenix, and the Mars Science Laboratory (MSL). Our results are most applicable to the Thermal and Evolved Gas Analyzer (TEGA) instrument on the Phoenix lander and the Sample Analysis at Mars (SAM) instrument on MSL but can be generalized to any instrument operated under similar non-standard conditions as compared to standard practice in terrestrial labs. This work provides a framework to interpret data returned from these missions and compare them to the existing library of terrestrial thermal analysis literature.

Although other techniques such as X-ray diffraction are better suited for definitive mineral identification of crystalline minerals of relatively high abundance, the high sensitivity of TA instruments (particularly those that include sensitive evolved gas analysis [EGA] capabilities) makes thermal analysis a useful technique in detecting volatile-bearing minerals down to very low abundances. Furthermore, thermal analysis can detect volatile bearing species with no long range order—referred to as X-ray amorphous materials—that cannot be identified by X-ray diffraction (XRD). As stated previously, mineral identification by thermal analysis is done by comparing results with the library of results that have been built up over the history of TA work. Caution is required when comparing results from Mars with previous TA work because instrument conditions such as pressure, heating rate, and carrier gas effects, as well as sample properties such as total sample mass and particle size, can affect thermal decomposition behavior [4-8]. Therefore, the standard approach to identifying minerals based on data from Mars has been to run analog samples under instrument conditions that replicate conditions on Mars [9]. This approach can be problematic because the number of flight-like instruments is small and, therefore, sample throughput is low and does not lend itself well to timely sample identification. Rapidly identifying probable minerals present in a sample is important on a mission such as MSL where information about a particular sample might make the difference between more investigation or moving on to another area.

This work has two primary goals that will aid in sample identification. The first is to investigate whether or not an analytical or empirical relationship exists between experimental conditions (primarily pressure) and thermal decomposition temperature. If such a relationship could be established, the large body of existing thermal analysis literature done under terrestrial standard conditions could be scaled and compared to results from Mars, reducing the need to analyze a large number of possible minerals under Mars-relevant instrument conditions. The second objective is to investigate the effects of carrier gas (both species and flow rate)

and sample particle size on thermal decomposition behavior. The magnitude of these effects will determine the feasibility of developing a predictive model.

Thermal analysis on Mars

Thermal analysis has been used three times on past Mars missions (one instrument on each Viking lander, one on the Phoenix lander) and is currently being used by the Sample Analysis at Mars (SAM) instrument on board the Mars Science Laboratory (MSL) which landed on Mars in August 2012. Each Viking lander carried a Gas Chromatograph/Mass Spectrometer (GCMS) that flash heated a sample to release volatile compounds. Although the Viking ovens flash heated samples to 50, 200, 350, and 500°C, giving some information regarding when various gases evolved, a direct line from the oven to the mass spec was removed to reduce complexity and cost. This greatly limited information about the evolution temperatures of detected gases and consequently, although CO_2 was detected by both landers that could have been due to the decomposition of carbonates, a definitive identification could not be made [10]. Because of these limitations, the experimental conditions used in our work are chosen to more closely approximate the TEGA and SAM instruments and will be most useful in analyzing data from those instruments.

The TEGA instrument on the Phoenix lander consisted of eight ovens that could heat a sample at a controlled ramp rate of 20°C/min to release gas from volatile-bearing minerals, as well as any organics present, with the evolved gas being measured by a mass spectrometer. TEGA also made calorimetric measurements of samples during heating [11]. The TEGA instrument detected a high temperature CO_2 release (>700°C) with an accompanying endotherm in the calorimetry data. Coupled with data from the Wet Chemistry Laboratory (WCL), which measured a soil pH of 7.7 ± 0.5 [12], the release of CO_2 was interpreted to be due to 3-5% calcite in the sample [9,11].

The SAM instrument on MSL has a primary goal of determining the present and past habitability of Mars—and specifically the selected landing site at Gale Crater—by searching for organic material relevant to life and mineralogy indicative of past or present habitable conditions [13]. SAM will analyze soils or powdered rock by controlled rate pyrolysis (and flash heating of a hydrocarbon trap for gas chromatography), with evolved gases being measured by a quadrupole mass spectrometer. In addition to detecting any organic molecules present, evolved gases and their evolution temperatures will be used to identify volatile bearing minerals in martian samples in concert with complementary instruments. Gale crater was selected as the MSL landing site in part for its access to phyllosilicates and sulfate minerals detected from orbit [14]. The SAM instrument will be used to perform a sensitive search for those minerals, as well as carbonates and any other volatile-bearing minerals. Identifying the presence and abundance of these minerals is an important step in quantifying the present and past habitability of a specific location on Mars.

Thermal analysis

Thermal analysis can be used to identify minerals by a few different methods. First, differential scanning calorimetry (DSC) measures heat flow into or out of a

sample compared to a reference and uses the endo- or exotherms associated with decomposition or phase changes as diagnostic of a given material (Endothermic reactions require energy and the heat flow into the sample is greater than into the reference to achieve a given temperature. Exothermic reactions release heat and the sample crucible requires less energy than the reference). For example, calcite is a very common mineral used in thermal analysis, in which calcium carbonate ($CaCO_3$) decomposes to lime (CaO) and CO_2 at high temperatures. The decomposition reaction is endothermic—requiring about 170 kJ/mol—and occurs at a characteristic temperature of around 800°C under standard terrestrial laboratory conditions. The weight of the sample can also be dynamically measured by thermal gravimetric analysis (TGA). Calcite decomposition leads to a ~44% weight loss in a single event. If the gases released during thermal decomposition are monitored (EGA), a large release of CO_2 will be seen concurrent with the weight loss and endotherm in the TG/DSC data. In a sample of unknown composition, observing these DSC, TG, and EGA signatures together would be a strong case for the presence of calcite. This illustrates how comparing thermal analysis results to TA measurements of known materials can be used to identify minerals in samples of unknown mineralogy.
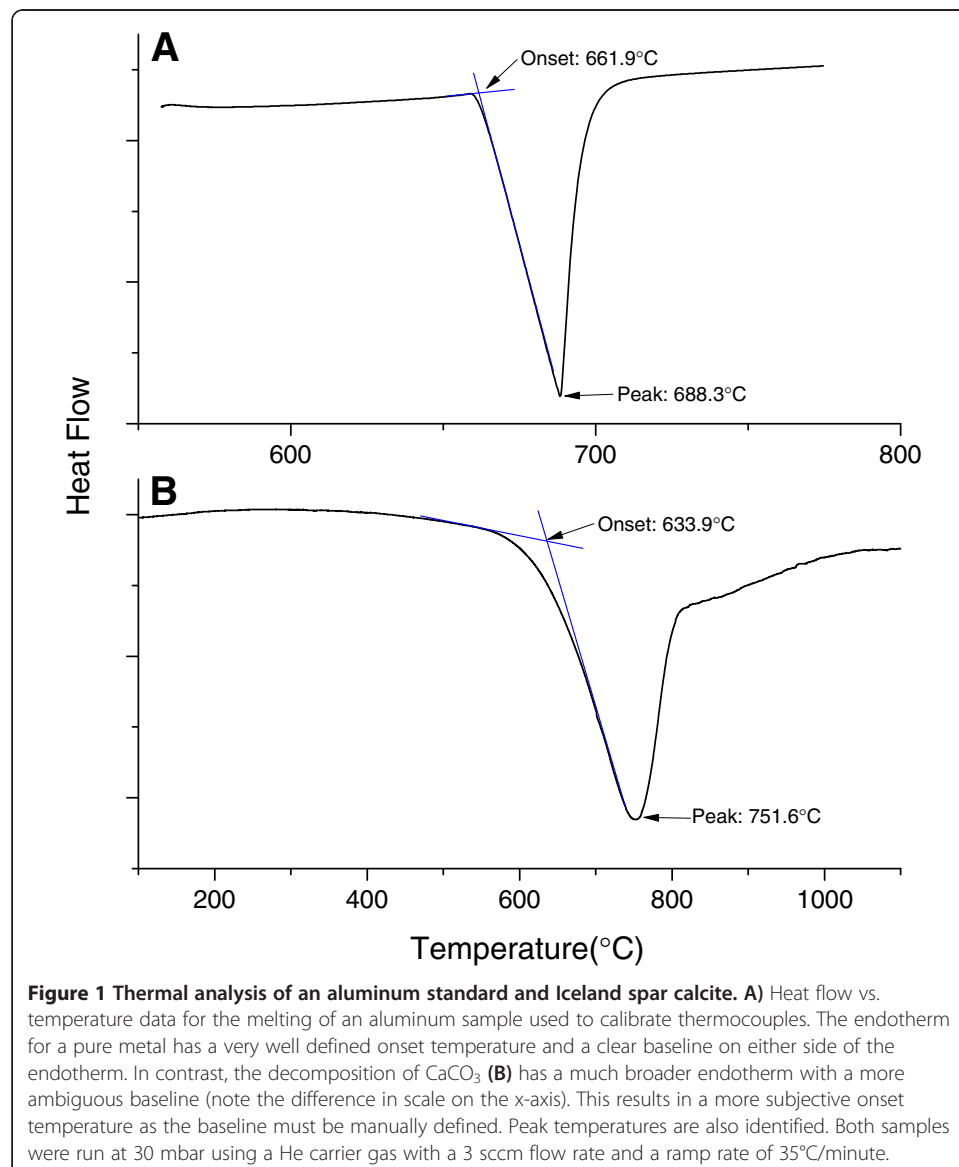
Although some decomposition behavior can be predicted based on thermodynamic or the decomposition reaction itself (i.e. enthalpy of reaction, mass loss, gas evolved, etc.), comparison to known standards run under similar conditions is necessary because other factors, particularly the decomposition temperature, are determined by a number of parameters such as the pressure of the chamber where decomposition occurs or the particle size of the sample. Simultaneous DSC, TGA, and EGA measurements can mitigate some of these complicating factors by providing additional lines of evidence; however, no thermal analysis instrument flown to Mars (including SAM) has included a full suite of thermal analysis capabilities (Table 1). Therefore, quantifying the effects of instrument conditions and sample physical properties on decomposition temperature is crucial in correctly interpreting data from Mars. We describe how decomposition temperature changes with different instrument and sample conditions by using simultaneous DSC, TGA, and EGA, and identify important factors that must be taken into account when interpreting spacecraft data.

Table 1 Mars spacecraft thermal analysis instruments

	GC/MS (Viking)	TEGA (Phoenix)	SAM (Mars science laboratory)
Landing date	July 20, 1976 (Viking 1)	May 25, 2008	August 6, 2012
	September 3, 1976 (Viking 2)		
Thermal analysis capabilities	EGA	EGA, DSC	EGA
Flow rate (sccm)	1.5-2.5	1.7	1.5
Instrument pressure (mbar)	not reported	12	30
Carrier gas	H_2 or CO_2	N_2	He
Ramp rate (°C /minute)	Flash heating	20	35

Decomposition temperature

The decomposition temperature of a mineral can actually refer to two different temperatures that can be measured and used to characterize a sample: the onset and the peak temperature. The onset temperature is defined by the intersection of a line tangent to the baseline with a line tangent to the inflection point of the DSC heat flow curve, where the first derivative of the heat flow curve is a maximum (Figure 1). Decomposition onset temperatures for volatile bearing minerals (Figure 1B), even a relatively pure natural calcite sample, are not nearly as straightforward as those for high purity metals used to calibrate TA instruments (Figure 1A). Unlike the phase change (e.g. melting) of a high purity metal, the onset temperature of decomposition reactions of volatile bearing minerals can be affected by things such as instrument pressure and sample particle size. For more complex samples, decomposition stretches out over a wide temperature range and the idea of a single onset temperature is more conceptually difficult to define.

Figure 1 Thermal analysis of an aluminum standard and Iceland spar calcite. A) Heat flow vs. temperature data for the melting of an aluminum sample used to calibrate thermocouples. The endotherm for a pure metal has a very well defined onset temperature and a clear baseline on either side of the endotherm. In contrast, the decomposition of $CaCO_3$ **(B)** has a much broader endotherm with a more ambiguous baseline (note the difference in scale on the x-axis). This results in a more subjective onset temperature as the baseline must be manually defined. Peak temperatures are also identified. Both samples were run at 30 mbar using a He carrier gas with a 3 sccm flow rate and a ramp rate of 35°C/minute.

The peak temperature can also be used to identify a mineral during thermal analysis, where "peaks" are defined as local maxima or minima in DSC data, maxima in EGA data, and maxima in the first derivative of TG data. When a decomposition reaction has a DSC, EGA, and TG peak, temperatures between the three data types roughly coincide. Because DSC and TG data are generally measured by the same instrument, the agreement between the two peaks should be very good. How well the EGA peaks coincide is a function of the instrumental setup as evolved gases must travel from the furnace to the mass spectrometer to be detected. Peak temperature is much more straightforward to measure but is difficult to predict as it depends on the kinetics of the reaction as well as sample size rather than equilibrium thermodynamics.

Onset and peak temperatures are defined based on heat flow data as opposed to evolved gas data because DSC is a more widely used thermal analysis technique due to its versatility (DSC can measure phase changes, specific heats, etc.). In this work, onset and peak temperatures are calculated from DSC data; however, we have found that EGA vs. DSC peak temperatures only differ by 5-10% at low pressure and can essentially be used interchangeably.

Methods

The Astromaterials Research and Exploration Science (ARES) Directorate at the NASA Johnson Space Center has developed state of the art thermal analysis testbeds to simulate instrumental conditions of the TEGA and SAM instruments. Samples were run in a Netzsch STA 449 F1 Jupiter with simultaneous TG/DSC capability. This instrument consists of a furnace to heat the sample at rates up to 50°C/min (this particular instrument is equipped with a silicon carbide furnace capable of heating samples to 1550°C), a balance chamber that measures changes in sample mass during heating (TG), and a sample carrier that holds the sample and reference crucibles and measures the temperature of each to compute the difference in heat flow into the two cups (DSC). The instrument can be configured to use a variety of carrier gases, necessary to sweep evolved gases out of the oven and balance chamber for further analysis and instrument safety reasons (e.g. to remove corrosive gases). Helium and nitrogen were used as carrier gases for this work. A Pfeiffer Thermostar GSD 320 with a 1-200 AMU range PrismaPlus quadrupole mass spectrometer is coupled to the gas output of the TG/DSC for evolved gas analysis via a 500 μm inner diameter glass-lined stainless steel capillary. The entire path-length of the gas is heated to ≥200°C to prevent gas condensation in the line before analysis. The Pfeiffer mass spectrometer was used in a mode that measures the peak value at each mass number from 1-100 AMU. One complete scan takes from 5-7 seconds to complete and experience has shown that this is sufficiently good time resolution to catch evolved gas peaks as one run takes on the order of an hour to complete. The SEM (secondary electron multiplier) detector was used during analysis due to its high sensitivity. The carrier gas signal was between 10^{-6} and 10^{-8} A (ion current) and the noise floor of the SEM is ~10^{-13} resulting in a sensitivity of 1 part in 10^7 or 1 in 10^5, depending on the instrument oven pressure.

Samples were run at instrument pressures of 12, 30, 150, and 1000 mbar. These values were chosen because they correspond to TEGA (12 mbar), SAM (30 mbar), and the terrestrial standard (1000 mbar), as well as an intermediate value between the

two pressure regimes (150 mbar). Pressure was monitored by a gas-independent capacitance pressure gauge.

Instrument temperature was calibrated by heating indium (melting point = 156.6°C), tin (231.9°C), lead (327.5°C), aluminum (660.3°C), and gold (1064.2°C) past their melting points, and using the measured vs. actual melting points to derive coefficients for a temperature correction equation that is applied to subsequent scans. The melting point of the metals used spans almost the entire temperature range of the instruments, insuring accurate temperature measurements for all of the samples run. Temperatures were calibrated at 5, 20, and 35°C/minute ramp rates at different pressures because both of these parameters affect the measured temperatures. Heat flow measurements were calibrated by heating a sapphire disc at 20 and 35°C/minute from ambient to 1400°C and comparing the measured heat flow to accepted standard values. This method converts raw data (reported in volts) to be converted to power (watts), which is used to determine reaction or phase change enthalpies. This calibration was also done at each pressure used in our experiments.

Compositions and provenance of samples used in this study are listed in Table 2. Samples were chosen based on the following criteria:

1) They undergo some type of thermal decomposition below 1450°C (the upper temperature limit of our oven at low pressure).
2) The samples collectively have decomposition temperatures that both span the entire temperature range of our instrument and do so at relatively regular intervals so that the entire temperature range was well sampled.
3) They have been detected on Mars or have been proposed as minerals likely to be present.

Samples with particle sizes of <150 μm were used for analysis, with the exception of our investigation of particle size effects. Samples with an initial particle size >150 μm were ground in a mortar and pestle until all material passed through a 150 μm sieve. To investigate the effects of particle size on decomposition behavior, samples of kaolinite and calcite were prepared differently, in addition to being prepared as <150 μm samples. Samples of a Clay Minerals Society kaolinite standard (KGa-2) were sorted into different particle size separates by sieving for the >53 μm size fraction and Stokes Law settling to separate particles into < 2 μm and 2-53 μm size fractions. No grinding was needed for KGa-2 as it comes as a pre-powdered sample already containing small particle size material.

Table 2 A list of the samples used in this work, including composition, mineral type, and the source of the sample

Sample name	Chemical composition	Mineral type	Source
Magnesite	$MgCO_3$	carbonate	Winchester, WI
Calcite	$CaCO_3$	carbonate	Iceland Spar Calcite from Wards Natural Science
Goethite	$FeO(OH)$	iron oxyhydroxide	Pfizer (YO- 3587, described by [15])
Kaolinite (KGa-2)	$Al_2Si_2O_5(OH)_4$	phyllosilicate	Clay Mineral Society standard
Ca-Montmorillonite (STx-1)	$Ca_{0.3}Al_2Si_4O_{10}(OH)_2 \cdot (H_2O)_{10}$	phyllosilicate	Clay Mineral Society standard
Kieserite	$MgSO_4 \cdot H_2O$	sulfate	K + S company, ESTA Kieserite
Epsomite	$MgSO_4 \cdot 7(H_2O)$	sulfate	Standard pharmacy grade
Alunite	$KAl_3(SO_4)_2(OH)_6$	sulfate	Wards Natural Science

Different particle size fractions of Iceland spar calcite were obtained by using a mallet and razor blade to chip crystals 2-3 mm a side off a much larger block of sample. These were the largest crystals that would fit in the crucibles used for TG/DSC. Some of this same material was then ground in a mortar and pestle to produce the 1-2 mm and 0.5 to 1 mm size fractions. Smaller particle size fractions were produced by grinding in a mortar and pestle with isopropyl alcohol added to reduce the possible formation of reactive surfaces during the grinding process [16,17]. The resulting powder was then wet sieved in isopropyl alcohol to obtain size fractions of 250-500 μm, 125-250 μm, 53-125 μm, and <53 μm. These samples were then immersed in isopropyl alcohol and sonicated, a process that suspends clay-sized particles that can adhere to larger grains. The liquid was poured off and replaced and the process was repeated several times until the isopropyl alcohol remained clear after sonication, indicating the effective removal of the smallest particle-size material.

Samples were placed into a 6.8 mm diameter by 4 mm tall cylindrical alumina crucible and weighed before each run. ~10 mg of sample was used in most cases as this was found to be enough sample to accurately measure decomposition behavior. Using similar amounts of sample each run eliminates possible effects of sample mass on decomposition temperature [8]. The exception to this is the 2-3 mm crystals of Iceland spar calcite where a single crystal weighed ~50 mg. The alumina crucibles used were washed in acid and baked at 1000-1100°C to clean them before use, though this was not done between runs of identical samples if the residue did not stick to the crucible because experience has shown that reusing a crucible does not affect results for these samples.

Samples were heated up to ~1100°C in most cases, which matches the maximum SAM oven temperature (depending on the oven used), is a little higher than the maximum TEGA temperature (1000°C), and is much higher than the Viking maximum (500°C). Particular samples were heated to 1450°C because some minerals of interest to Mars (Ca-sulfates for example) do not decompose until these high temperatures. Using higher temperatures than have/will be achieved on Mars is useful because it allows analysis of a wider range of samples, improving our understanding of the effects of instrument pressure, particle size, etc. Higher temperature data are also useful because they demonstrate which minerals are likely undetectable by instruments on Mars with lower maximum oven temperatures.

A carrier gas is used to sweep evolved gases from the furnace which can then be measured by a quadrupole mass spectrometer (QMS). Nitrogen and helium were used as carrier gases in our experiments to match the carrier gases used by the TEGA (N_2) and SAM (He) instruments. Carrier gas flow rates ranged from 1-20 sccm, depending on the experiment being conducted. Gas flow rates were monitored by a Sierra SmartTrak 2 Model 100 mass flow meter which has been calibrated to be accurate to ±1% in the mass flow range used in these experiments. The units for mass flow used in this paper are standard cubic centimeters per minute (sccm). Though the units seem to imply a volumetric flow measurement, it is the mass of the gas flow that is measured, converted to a volumetric rate by assuming standard temperature (25°C) and pressure (1 bar) conditions.

The TEGA instrument used a 20°C/minute ramp rate and 35°C/minute is used by SAM. Again, as our work is primarily in support of MSL, most of our runs

Table 3 Peak temperatures of DSC endotherms for all samples and all four oven pressures used, arranged in order of increasing peak temperatures at 1000 mbar

Sample	Decomposition type (source of gas released)	DSC peak temperature (°C)			
		12 mbar	30 mbar	150 mbar	1000 mbar
Epsomite	H_2O (structural H_2O)	94.2	107.9	103.1	127.8
Montmorillonite	H_2O (cation solvation water)	87.3	97.9	111.6	135.0
Goethite	H_2O (structural OH)	297.8	304.4	312.0	327.4
Kieserite	H_2O (structural H_2O)	392.7	394.8	395.4	404.4
Kaolinite	H_2O (structural OH)	503.6	506.3	509.5	524.7
Alunite	H_2O (structural OH)	563.4	564.3	566.9	570.0
Magnesite	CO_2 loss (carbonate decomposition)	595.0	605.3	615.3	628.6
Alunite	H_2O (structural OH)	631.8	637.1	642.6	642.3
Montmorillonite	H_2O (structural OH)	699.3	702.2	712.1	763.9
Alunite	SO_2 loss (sulfate decomposition)	767.6	766.1	769.2	782.6
Calcite (<150 μm)	CO_2 loss (carbonate decomposition)	719.0	736.2	766.2	807.0
Calcite (3 mm crystals)	CO_2 loss (carbonate decomposition)	933.7	938.3	954.9	971.7
Epsomite	SO_2 loss (sulfate decomposition)	951.9	972.3	1033.4	1105.7
Kieserite	SO_2 loss(sulfate decomposition)	1062.6	1081.8	1100.4	1162.1

Decomposition type shows what is being lost in the decomposition and measured by the EGA, with the source of the gas loss specified.

were carried out at 35°C/minute (exceptions will be noted). Phase changes and decompositions happen at higher temperatures with higher ramp rates, so the absolute values of some of our results would be lower at lower ramp rates. However, the general conclusions of this paper are equally valid for different ramp rates. Finally, each sample was run at least twice under a given set of conditions to quantify the repeatability of the decomposition behavior and to identify outliers. Error bars in plots are the standard deviation of the average values of multiple runs unless otherwise specified.

Results and discussion

Thermal decomposition peak temperatures for the minerals described above, run at 12, 30, 150, and 1000 mbar, are listed in Table 3. These data were used to investigate whether an analytical or empirical model could fit the data to predict how pressure affects thermal decomposition temperatures for other samples. They also show how kinetic effects that depend on factors such as sample size (<150 μm vs. 3 mm calcite samples) can effect thermal decomposition behavior.

Investigating an analytical model

n theory, the onset temperature is the temperature at which a chemical reaction should occur spontaneously from an equilibrium thermodynamics perspective (peak temperatures are kinetically controlled and coincide with the maximum decomposition reaction rate [3]). Expected onset temperatures can easily be calculated using the basic equation that defines the Gibbs free energy (G) in terms of enthalpy (H), temperature (T), and entropy (S):

$$\Delta G = \Delta H - T \Delta S$$

The reaction is spontaneous when $\Delta G = 0$ and the onset temperature is simply the change in enthalpy divided by the change in entropy of the products and reactants. However, onset temperature is seen to depend on pressure for gas-producing reactions (Figure 2, black data points). Because enthalpy is not pressure dependent, the change in onset temperature at lower pressures is due entirely to changes in ΔS. Again, from basic thermodynamics,

$$\Delta S \propto \ln \frac{V_f}{V_i}$$

Where V_f and V_i are the final and initial volume, respectively. Using the ideal gas law, we can substitute pressure for volume and find that

$$\Delta S \propto \ln \frac{P_i}{P_f}$$

Since we are calculating the change in entropy at lower pressures, P_i (terrestrial ambient) is always larger than P_f (final pressure) and, consequently, ΔS is always larger, leading to lower onset temperatures at lower pressures.
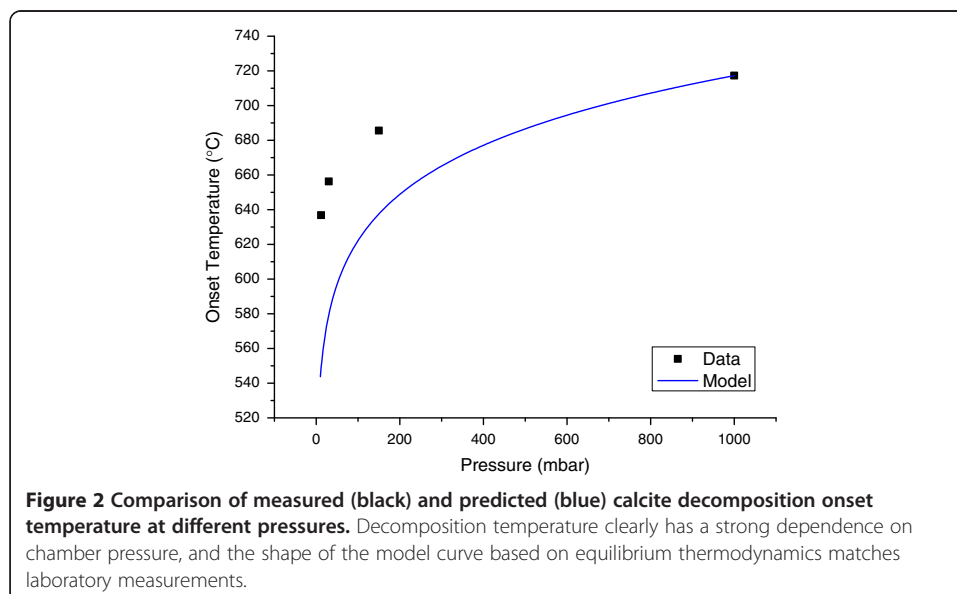
To derive an analytical model, we start with the equations

$$T_{HP} = \frac{\Delta H_{HP}}{\Delta S_{HP}}$$

and

$$T_{LP} = \frac{\Delta H_{LP}}{\Delta S_{LP}}$$

which is the onset temperature (when $\Delta G = 0$) for the decomposition reactions at high pressure (HP = 1000 mbar) and low pressure (LP = 150, 30, and 12 mbar in our runs). If

Figure 2 Comparison of measured (black) and predicted (blue) calcite decomposition onset temperature at different pressures. Decomposition temperature clearly has a strong dependence on chamber pressure, and the shape of the model curve based on equilibrium thermodynamics matches laboratory measurements.

we assume that reaction enthalpy is not pressure dependent ($\Delta H_{HP} = \Delta H_{LP}$ or ΔH for simplicity) and that $\Delta S_{LP} = \Delta S_{HP} + R \, ln(P_{HP}/P_{LP})$, where R is the ideal gas constant, we can solve for $T_{HP}\text{-}T_{LP}$ (ΔT) and find:

$$\Delta T = \frac{\Delta H R ln \frac{P_{HP}}{P_{LP}}}{\Delta S_{HP} + \Delta S_{HP} ln \frac{P_{HP}}{P_{LP}}}$$

Using this equation with measured values of reaction enthalpy $\Delta (H)$, and letting ΔS_{HP} be the reaction enthalpy divided by the onset temperature at 1000 mbar, we can predict the change in temperature as a function of instrument pressure (Figure 2). While the shape of the model curve (blue) is roughly the same, the model overpredicts the change in temperature with pressure, meaning that at a given pressure, the predicted decomposition temperatures are significantly lower than what is actually observed. Though only calcite data are shown here, the model also overpredicts the change in temperature with pressure for magnesite (>150°C difference), and the H_2O (~120°C difference) and SO_2 (~90°C difference) releases from kieserite decomposition.

Figure 3 Change in peak temperature at low pressure vs. peak temperature at 1000 mbar for the minerals listed in Table 3 (Ep = epsomite, Mo = montmorillonite, Go = goethite, Ki = kieserite, Ka = kaolinite, Al = alunite, Ma = magnesite, Ca (1) = <150 μm calcite, Ca (2) = 3 mm calcite). For example, the peak temperature of magnesite at 1000 mbar (x axis) is 629°C. The change in peak temperature (or ΔT, plotted on the y axis) is -13, -23, and -34°C at 150, 30, and 12 mbar, respectively. The difference in the Ca(1) and Ca(2) decomposition temperatures is due to particle size effects, discussed in detail in the main text. Ep, Ki, Mo, and Al appear multiple times in the plot because they decompose in multiple gas-releasing steps (e.g. epsomite releases water at low temperature and SO_2 from sulfate decomposition at higher temperature). This figure shows that, although there might be a small trend in increasing ΔT with peak temperature at 1000 mbar, the scatter in the data is large, making prediction based on these data difficult. Furthermore, the effects of sample particle size are as large as the effects of pressure, showing that a pressure-only model is not sufficient to predict the change in decomposition temperatures. Samples were run using a 3 sccm He carrier gas flow and a ramp rate of 35°C/minute.

Based on this analysis, it is clear that equilibrium thermodynamics alone are not sufficient to predict changes in onset temperature. This implies that kinetic factors such as differences in activation energy due to particle size differences must play a large role in decomposition behavior, including onset temperature. With knowledge of the properties of the sample to be analyzed, such as the amount of a given mineral present and its particle size, it may be possible to build a predictive model based on equilibrium and kinetic factors. However, past and current spacecraft instruments have not given us the level of detailed information necessary to make the model useful in predicting exact decomposition temperatures under different instrument conditions.
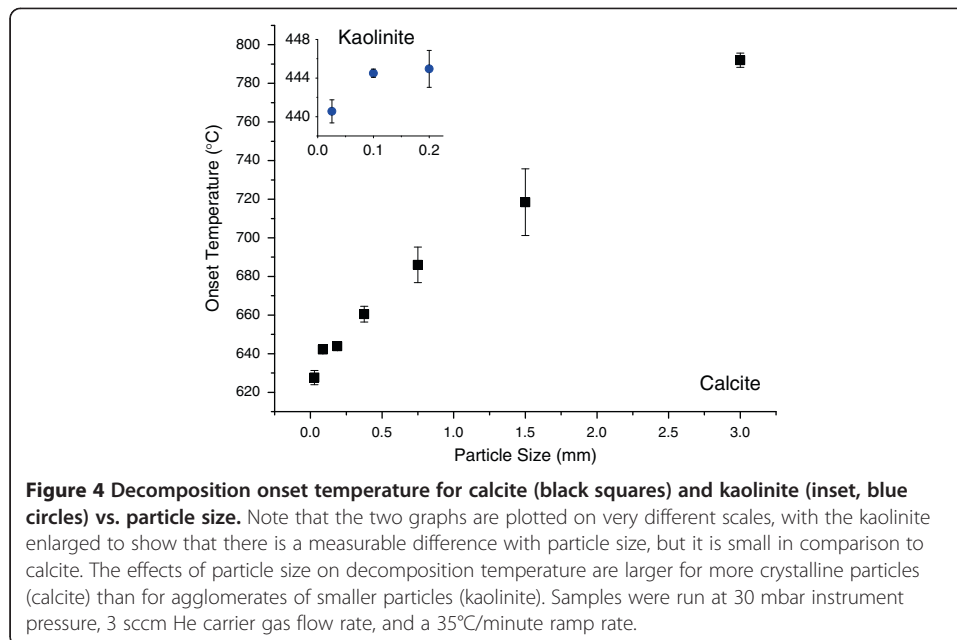
An empirical model

In addition to complicating the development of an analytical model to predict decomposition behavior under different instrument conditions, kinetic factors can have such varied effects on decomposition behavior that a useful empirical model is not straightforward. When plotting how the endotherm peak temperature changes with temperature for different minerals, as referenced to the peak temperature at 1000 mbar, no clear relationship is seen (Figure 3, minerals listed in Table 3). Though there may seem to be a slight relationship of increasing ΔT with increasing peak temperature, this relationship breaks down under further investigation. For example, <150 μm calcite is plotted at ~800°C at 1000 mbar with changes in decomposition temperature ranging from 40 degrees at 150 mbar to almost 90 degrees at 12 mbar. When large single crystals of calcite are run, the decomposition temperature at 1000 mbar increases to 970°C and the change with pressure decreases to 17°C at 150 mbar and less than 40°C at 12 mbar. Different sample particle sizes introduces another variable into the equation and shows that, similar to the analytical model, predicting the change in decomposition temperature with instrument pressure would require information about the sample before it was run (i.e. particle size) that was not well known for Viking, TEGA, or SAM.

Thus far, we have shown that an analytical model based on equilibrium thermodynamics and an empirical model based on many samples run under different conditions do not make accurate predictions about the change in decomposition temperature with changing instrument pressure. We postulate that this is due to, among other things, kinetic effects, and show an example of how particle size can affect decomposition temperature. The following sections are a more in-depth look at the how kinetic effects and other instrument parameters change decomposition behavior, concentrating primarily on particle size and carrier gas species and flow rate Although we have shown that developing a predictive model is problematic, it is still useful to explain in broad terms how instrument conditions and kinetic factors affect decomposition reactions because these insights provide invaluable information to those who wish to interpret data returned from instruments such as TEGA or SAM.

Kinetic effects
Particle size

The particle size of samples analyzed can have a large effect on decomposition temperatures (Figure 4). For the calcite sample, the onset temperature drops from almost 800°C down to close to 625°C as particle size drops from ~3 mm to <53 μm. The effect of

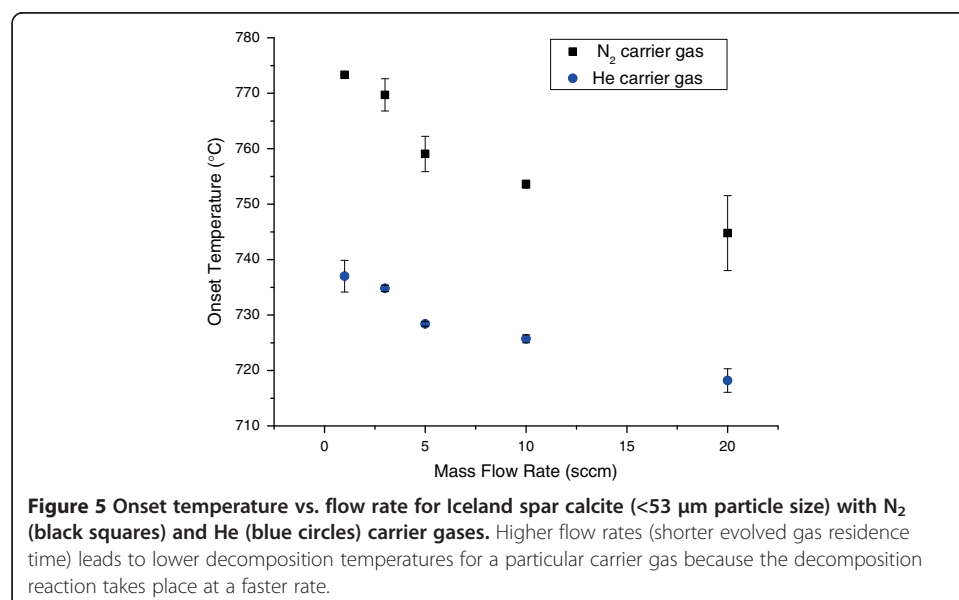**Figure 4 Decomposition onset temperature for calcite (black squares) and kaolinite (inset, blue circles) vs. particle size.** Note that the two graphs are plotted on very different scales, with the kaolinite enlarged to show that there is a measurable difference with particle size, but it is small in comparison to calcite. The effects of particle size on decomposition temperature are larger for more crystalline particles (calcite) than for agglomerates of smaller particles (kaolinite). Samples were run at 30 mbar instrument pressure, 3 sccm He carrier gas flow rate, and a 35°C/minute ramp rate.

particle size on the KGa-2 kaolinite sample, run under the same conditions, is much less pronounced, showing a difference of only ~4°C from the >150 μm size fraction to the 2-53 μm size fraction (Figure 4). This much smaller difference illustrates the role of crystallinity in particle size effects, another variable which can influence decomposition behavior. The calcite particles were all mono-crystalline as they were produced by breaking small pieces off of a large crystal and subsequently grinding those pieces to smaller sizes. The larger particles of KGa-2, a clay mineral, are composed of agglomerates of smaller crystals, so although the particle size of agglomerates varies, the size of the crystallites in each agglomerate is roughly the same, leading to much smaller differences in decomposition behavior for samples of different particle size.

While the effects of sample particle size on the decomposition temperature of many reactions have long been known [2], the exact mechanism for why this occurs remains poorly understood. Possible explanations include decreasing activation energy with decreasing particle size due to increased surface area that provides extra energy stored on particle surfaces [18,19] or a dependence on evolved gas diffusion rates out of the parent material (slower diffusion out of larger particles would lead to a buildup of reaction products, slowing the forward reaction rate and leading to higher decomposition temperatures) [20]. Regardless of what causes the differences in decomposition behavior, particle size effects cannot be ignored. Because minerals release a very limited number of gas products, primarily H_2O, CO_2, and SO_2, decomposition temperature is used to differentiate between minerals. Even if the effects of instrument pressure are taken into account, ignoring the possible effects of particle size could, for example, result in confusing small particles of calcite with larger particles of magnesite (which both give off CO_2 within ~100°C of each other). This example illustrates the pitfalls of overreliance on TA data for exact mineral identification and demonstrates the importance of understanding how sample physical properties, such as particle size, can affect thermal decomposition results.

Carrier gas species and flow rates

The carrier gas used and instrument flow conditions are also important factors affecting decomposition behavior. Terrestrial systems generally use high flow rates (20 to 100 sccm) because they are not constrained by the total gas supply. Planetary instruments cannot carry an infinite supply of gas and therefore use much lower flow rates (see Table 1). However, comparing flow rates directly is not sufficient because it does not take into account the different geometries of the instruments involved. Two gas systems could use the same flow rate, but different oven volumes (which can easily vary by an order of magnitude between different commercial systems) will lead to different decomposition results, even with all other parameters being the same. This is because the residence time of evolved gases in the reaction volume, not simply the flow rate, affects the decomposition behavior (the reaction volume is defined as the volume inside the instrument where gases can interact with the sample). The residence time depends on the flow rate, but also takes into account instrument geometry. The temperature at which calcite decomposes to CO_2 and lime, for example, depends strongly on the flow rate of the gas used. Decomposition temperatures drop by 20-30°C in both N_2 and He carrier gases when flow rates increase from 1 to 20 sccm (Figure 5). The higher decomposition temperature at lower flow rates is due to evolved CO_2 lingering in the system, slowing down the forward decomposition reaction.

The effects of residence time must be taken into account when comparing results between different instruments. The residence time in the oven is calculated by dividing the volume of the oven by the volumetric flow rate. The volumetric flow rate is the standard mass flow rate (reported in volumetric units such as sccm) multiplied by the quotient of standard pressure conditions (1 bar) over actual pressure conditions. The SAM instrument has an oven volume of 6 cm^3 and a volumetric flow rate of 0.6 cm^3/sec, giving a residence time of 10 seconds. When configured to approximate SAM, the Netzsch instrument is run with a 30 mbar He atmosphere and a gas flow rate of 3 sccm or an actual volumetric flow rate of 1.7 cm^3/sec (conversion
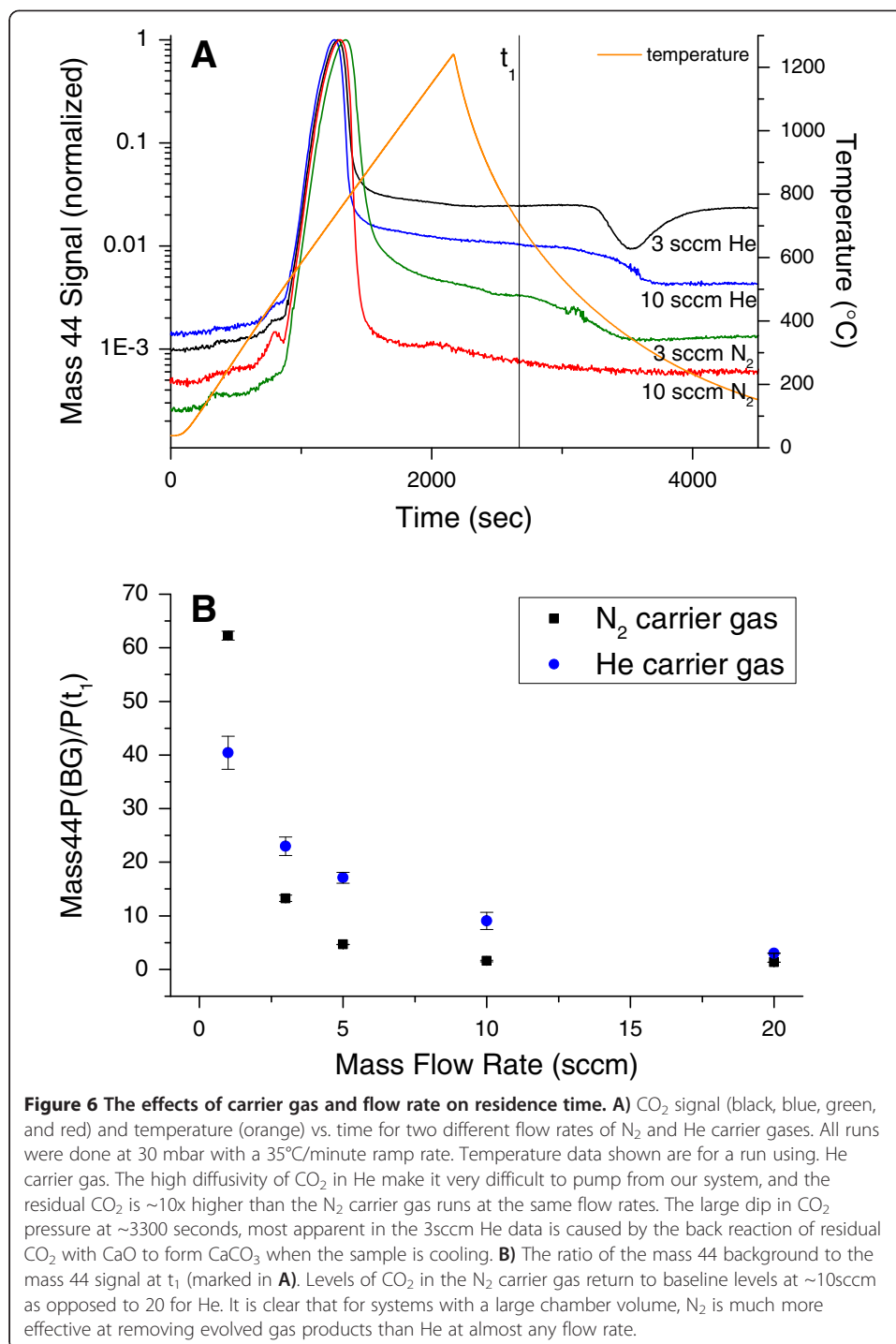
Figure 5 Onset temperature vs. flow rate for Iceland spar calcite (<53 μm particle size) with N₂ (black squares) and He (blue circles) carrier gases. Higher flow rates (shorter evolved gas residence time) leads to lower decomposition temperatures for a particular carrier gas because the decomposition reaction takes place at a faster rate.

from sccm to an actual volumetric flow rate: 3 sccm × 1 min/60 sec × 1000 mbar/30 mbar = ~1.7 cm^3/sec). Given a furnace volume of ~100 cm^3, the residence time of gas in the Netzsch instrument is ~60 seconds. So even though the mass flow rates of the Netzsch (3 sccm) is twice that of the SAM instrument (1.5 sccm), the Netzsch instrument has a residence time six times that of the SAM instrument due to its larger oven volume, a factor that must be taken into account when comparing data between the two instruments. To best reproduce conditions (and therefore measurements) of another instrument, gas flow rates should be scaled to produce similar residence times. Reproducibility should be assessed by running similar (or the same) materials in different instruments and comparing the results.

The specific carrier gas used can also affect the residence time of evolved gas in the system, depending on the geometry of the instrument used. Ideally, the residence time should not depend on the specific gas used because it depends only on volumetric flow rates (residence time = reaction volume divided by the volumetric flow rate). However, this is not necessarily true in practice and the degree of difference depends on which gases are used and the particular instrument geometry. For example, CO_2 evolved during calcite decomposition has a much longer residence time in our instrument when He is used as a carrier gas as opposed to N_2. Residual CO_2 is higher when He is used as a carrier gas at both 3 and 10 sccm compared to N_2 at the same flow rates (Figure 6). This is due to the much higher diffusivity of CO_2 in He compared to N_2 and the specific geometry of our instrument (the diffusivity of CO_2 in He is ~4 times higher than the diffusivity of CO_2 in N_2 at 20°C [21]). Though the furnace volume of the Netzsch instrument is relatively small (~100 cm^3), there is a small orifice connecting the furnace to the balance chamber, which has a much larger volume of ~1500 cm^3. The high diffusivity of CO_2 in He allows some of the evolved carbon dioxide to leak into the balance chamber, increasing the volume of gas that needs to be replaced and leading to much longer residence times. This higher residence time can in turn affect decomposition temperatures.

The magnitude of this effect must be characterized for each instrument because it depends on each instrument's particular geometry. For example, when using another instrument in our lab with a much smaller oven volume (~5 cm^3) and no connected larger volume, residence time is largely gas independent (at similar flow rates and instrument pressure). Overall, residence time will be carrier gas independent for systems with small oven volumes but can vary substantially for systems with larger volumes. The TEGA and SAM instruments both have small oven volumes so the specific carrier gas used should not affect decomposition behavior, although residence time will still play a role. The magnitude of this effect will need to be measured for systems whose results will be compared to Mars instruments to determine if residence time effects must be taken into account.

Even in instruments where diffusivity concerns are not an issue, evolved gas residence time is an important factor in thermal decomposition. As stated previously, the residence time of evolved gas (CO_2 in the case of calcite decomposition) can slow the forward reaction rate, affecting onset and peak temperatures. In a dynamic system where incoming gases are continuously pumped out, the rate of gas flow is proportional to the mass loss from the sample and controls the pressure of the gas in the system. Therefore, the equilibrium CO_2 pressure can be compared to the mass loss rate to
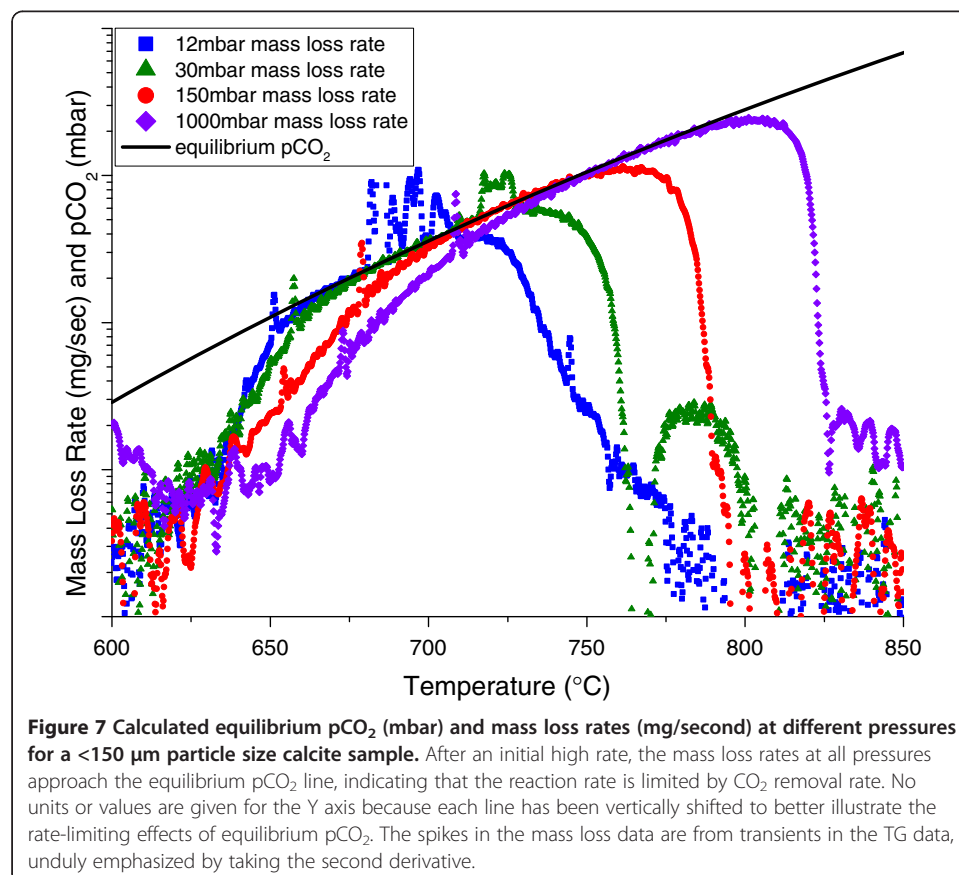
Figure 6 The effects of carrier gas and flow rate on residence time. A) CO_2 signal (black, blue, green, and red) and temperature (orange) vs. time for two different flow rates of N_2 and He carrier gases. All runs were done at 30 mbar with a 35°C/minute ramp rate. Temperature data shown are for a run using. He carrier gas. The high diffusivity of CO_2 in He make it very difficult to pump from our system, and the residual CO_2 is ~10x higher than the N_2 carrier gas runs at the same flow rates. The large dip in CO_2 pressure at ~3300 seconds, most apparent in the 3sccm He data is caused by the back reaction of residual CO_2 with CaO to form $CaCO_3$ when the sample is cooling. **B)** The ratio of the mass 44 background to the mass 44 signal at t_1 (marked in **A)**. Levels of CO_2 in the N_2 carrier gas return to baseline levels at ~10sccm as opposed to 20 for He. It is clear that for systems with a large chamber volume, N_2 is much more effective at removing evolved gas products than He at almost any flow rate.

determine if the CO_2 removal rate was the reaction limiting step. The CO_2 equilibrium pressure is calculated at different temperatures using the following equation:

$$P = e^{\frac{T\Delta S - \Delta H}{RT}}$$

where ΔS is 169 J/mol K and ΔH is 178.5 kJ/mol [22]. If the sample decomposition rate is limited by equilibrium pCO_2 (where pCO_2 is the partial pressure of CO_2), the slope
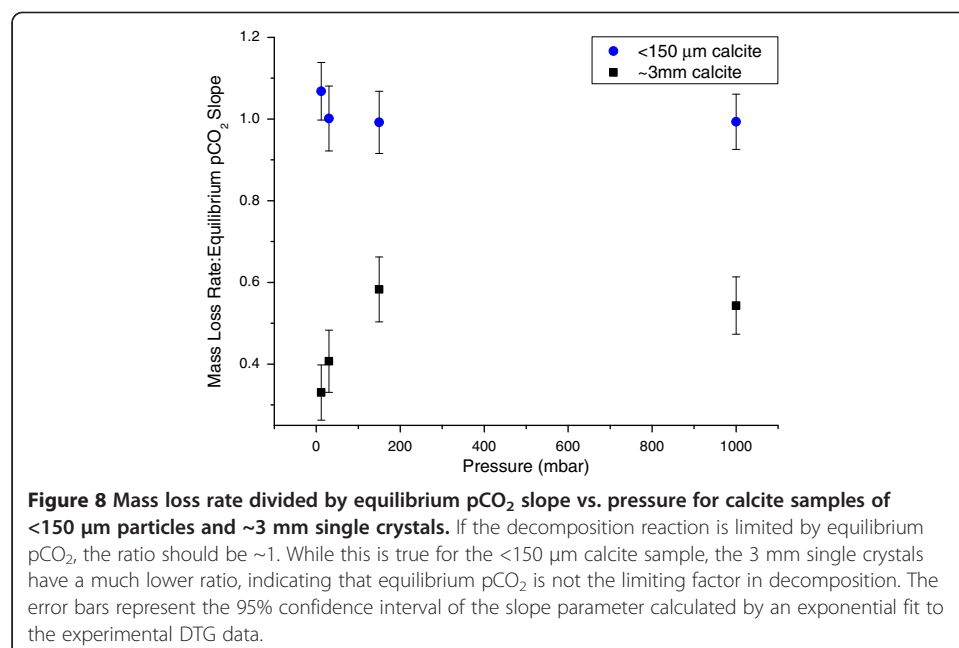
of the mass loss rate will approach but not exceed pCO_2 (Figure 7). The partial pressure of CO_2 in our vacuum system is controlled by the balance of how much gas is being produced (measured by the mass loss rate of the sample that is producing the gas) and how much gas is being removed from the system by the vacuum pumps, which is why pCO_2 can be compared to the mass loss rate. Comparing pCO_2 and the mass loss rate (the first derivative of the thermal gravimetry data, called differential thermal gravimetry or DTG), shows that for a calcite sample with particle sizes <150 μm, the decomposition rate is limited by pCO_2 or, in other words, the rate of CO_2 removal from the system. After a high initial slope, the slope of the mass loss rate quickly approaches the slope of the equilibrium pCO_2 based on thermodynamic principles. This clearly demonstrates that, under these instrument conditions and for this sample, the partial pressure of CO_2 is limiting calcite decomposition rates. This clearly indicates the importance of residence time on decomposition temperatures. Instruments with long residence times will result in higher decomposition temperatures as the decomposition reaction is slowed by a high concentration of reaction products. These data also demonstrate again that increasing instrument pressure increases the thermal decomposition temperature.

Although pCO_2 is clearly the rate-limiting factor for the prior sample, this is not always the case, as a different size fraction of the same sample gives different results. When comparing the slope of the mass loss rate (before it starts rolling over when the

Figure 7 Calculated equilibrium pCO_2 (mbar) and mass loss rates (mg/second) at different pressures for a <150 μm particle size calcite sample. After an initial high rate, the mass loss rates at all pressures approach the equilibrium pCO_2 line, indicating that the reaction rate is limited by CO_2 removal rate. No units or values are given for the Y axis because each line has been vertically shifted to better illustrate the rate-limiting effects of equilibrium pCO_2. The spikes in the mass loss data are from transients in the TG data, unduly emphasized by taking the second derivative.

supply of the original mineral is nearly exhausted) to the slope of the equilibrium pCO_2 line, the ratio should be ~1 if pCO_2 is the rate-limiting factor. To ensure we are comparing slopes at consistent temperatures, all slopes for the calcite samples are taken from a portion of the curve centered ~50°C before the peak slope value and are compared to the slope of the pCO_2 curve at the same temperatures. Plotting these values vs. pressure for two different size fractions of Iceland spar calcite (Figure 8) show that while pCO_2 is the limiting factor in calcite decomposition for the <150 μm calcite particles, the decomposition rate for the 3 mm size calcite sample never approaches the limit set by equilibrium pCO_2. Clearly, the decomposition reaction of these large calcite crystals is not limited by CO_2 removal from the system, but is instead limited by another kinetic factor such as the effects of self-cooling during decomposition, diffusion of CO_2 out of the sample itself, or by the much smaller surface area of calcite available in the larger sample [5,23]. Whatever the cause, the change in particle size of the sample has a dramatic effect on decomposition behavior, and can completely change the rate limiting step of the reaction.

A final point to consider is that lingering gas products can also have another important effect: if gas removal rates are slow enough that substantial gas products remain when the sample is cooling off, reactions can occur between the gas product and the remaining solid residue. In the case of calcite decomposition to lime—which is a reversible reaction—calcite formation during the cooling phase is observed in the TG/DSC/EGA data if there is sufficient residual CO_2 in the reaction chamber [24]. Calcite formation is indicated by a sharp drop in CO_2 abundance, seen in the dip in CO_2 in the 3 sccm He data at ~3500 seconds (Figure 6A), which corresponds with an exotherm in DSC data (not shown). This effect may not be entirely negative as it might differentiate a low-temperature calcite release from organic combustion. For example, if a ~500°C CO_2 release is

Figure 8 Mass loss rate divided by equilibrium pCO_2 slope vs. pressure for calcite samples of <150 μm particles and ~3 mm single crystals. If the decomposition reaction is limited by equilibrium pCO_2, the ratio should be ~1. While this is true for the <150 μm calcite sample, the 3 mm single crystals have a much lower ratio, indicating that equilibrium pCO_2 is not the limiting factor in decomposition. The error bars represent the 95% confidence interval of the slope parameter calculated by an exponential fit to the experimental DTG data.

detected with no complementary data to corroborate carbonate decomposition, the CO_2 release could also be due to organic combustion. However, if the original CO_2 producing material was a carbonate and enough carbon dioxide lingers in the system, a carbonate could reform during cooling, which would be seen as a sudden decrease of CO_2 in the EGA data. This would not occur if the CO_2 source was organic combustion and could provide a way to differentiate between the two possible CO_2 sources.

Conclusions

We have shown that physical properties of the sample such as particle size, carrier gas composition and flow rate, as well as the geometry of the instrument used, have a large effect on the temperature of a decomposition reaction. The large difference in decomposition temperatures that can be caused by these effects demonstrate the difficulties in developing an analytical model that predicts the change in onset temperatures for minerals under low pressure based on equilibrium thermodynamic properties. However, the fact that the overall shape of the predicted difference in onset temperature is similar demonstrates that equilibrium thermodynamics does predict the measured changes in decomposition temperature to some degree. Furthermore, although there appears to be a loose trend of an increase in the difference of decomposition temperature at different pressures as the decomposition temperature under terrestrial conditions increases, there is no good empirical fit to the data that would permit predicting the change in decomposition temperature at different pressures. Because the magnitude of these effects can be as large or larger (depending on the mineral) than the effect of pressure alone, a model that only depends on pressure will not be able to accurately predict the change in decomposition temperatures expected from samples run in instruments on Mars. Despite the difficulties in developing a predictive model, it is vitally important to understand the effects of these factors when interpreting data from planetary instruments since Mars data will be compared to results gathered under more traditional laboratory conditions.

Given the limitations we describe, the existing body of terrestrial literature regarding thermal decomposition behavior of minerals is still a useful starting point for additional study. When data are returned from Mars, they can be compared to terrestrial data that inform the selection of minerals to be run in testbed instruments. To best reproduce results obtained on Mars, these testbed instruments will need to have run the same (or very similar) samples that were run in flight (FM) or engineering qualifying models (EQM) of the instruments on Mars. Since each flight instrument is essentially unique (with perhaps the exception of an EQM) and imitating the exact Mars/spacecraft environment is difficult at best, reproducing the exact instrument conditions in the lab is not feasible. By running the same samples in testbed instruments that were run in FM or EQMs, the differences in decomposition behavior can be measured and explained, allowing for more confident identification of unknown minerals measured *in situ*. Fortunately, the SAM instrument carries a known mineral standard (calcite) that will be measured on Mars. This measurement will be invaluable in calibrating testbed instruments that will attempt to reproduce the results obtained on Mars to identify unknown minerals.

Thermal analysis has been and will continue to be a useful tool in identifying volatile-bearing minerals on Mars. Used in conjunction with spectroscopic measurements of Gale Crater (with typical detection limits of 1-3%+, much higher for certain minerals such as kaolinite [25-28]), and measurements by other instruments on MSL such as CheMin (~3% detection limit [29]), ChemCam, and APXS, the Sample Analysis at Mars instrument will be particularly useful in detecting trace amounts of volatile-bearing minerals. Correctly interpreting these data will require an understanding of how instrument effects and sample properties influence thermal decomposition behavior, as outlined in this paper.

Abbreviations

APXS: Alpha particle x-ray spectrometer; ARES: Astromaterials research and exploration science directorate; ChemCam: Chemistry & camera; CheMin: Chemistry & mineralogy; DSC: Differential scanning calorimetry; DTG: Differential thermal gravimetry; EGA: Evolved gas analysis; EQM: Engineering qualification model; FM: Flight model; GCMS: Gas chromatograph/mass spectrometer; MFC: Mass flow controller; MSL: Mars science laboratory; SAM: Sample analysis at Mars; sccm: Standard cubic centimeters per minute; SEM: Secondary electron multiplier; TA: Thermal analysis; TEGA: Thermal and evolved gas analyzer; TG/TGA: Thermal gravimetry or thermal gravimetric analysis; XRD: X-ray diffraction.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

DA carried out the work described in this paper and drafted the manuscript. DM and BS helped train DA in use of thermal analysis instruments, gave direction to the work, and edited the manuscript drafts. All authors read and approved the final manuscript.

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